

**RESEARCH ARTICLE****PETROLEUM HYDROCARBON UNDERGROUND WATER BIOREMEDIATION USING DIRECT APPLICATION TECHNIQUE, OF A BIONUTRIENT: A NIGER DELTA CASE****Ohia, Nnaemeka and Iyiegbu, Hillary**

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ARTICLE INFO**Article History:**Received 14th, July, 2015
Received in revised form 23th,
July, 2015
Accepted 13th, August, 2015
Published online 28th,
August, 2015**Key words:**Direct application
technique;Finger printing; gas
chromatography; bioremediation;
bionutrients; persulphate oxidant;
Benzene, Toluene, Ethylbenzene,
and Xylenes (BTEX); Total
Petroleum Hydrocarbon and
Below detection limit (BDL).**ABSTRACT**

Operational and accidental spill of petroleum hydrocarbon and pollution of the ecosystem by the activities of the oil and gas industries cannot be over emphasized. The underground water has become the ultimate sink for most petroleum contaminants, such as Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX); Aliphatic and Polycyclic Aromatic Hydrocarbons (PAHs). These compounds degrade the quality of the underground water, and have become a serious environmental concern.

This study presents the use of direct application technique, over an activated persulfate oxidant (bionutrient) as an underground water bioremediation technique that may be employed in a variety of contaminated site or underground water bioremediation programs. This technique possess the ability to biodegrade significantly, the petroleum hydrocarbon contaminants fast and cost effectively. Underground water samples were collected from contaminated site, a set of physical, chemical and biological laboratory based analysis were carried out before and after remediation. After the remediation by direct application technique, a significant reduction of Total Petroleum Hydrocarbon (TPH), and BTEX profile was observed in the contaminated underground water to be below DPR intervention value and detection limit respectively. Gas chromatography fingerprints showing the peak of individual organic compounds were as well obtained for BTEX and TPH respectively.

Copyright © Ohia, Nnaemeka and Iyiegbu, Hillary., This is an open-access article distributed under the terms of the Creative Commons Attribution License, which permits unrestricted use, distribution and reproduction in any medium, provided the original work is properly cited.**INTRODUCTION**

The Niger Deltabas in has been one of the most studied basin because of the occurrence of vast deposits of petroleum resources and the current production of all Nigeria's oil and gas is derived from this region (Nwilo and Badejo., 2005).

Water is apparently everywhere: streams, rivers, lakes, ponds, snow, oceans, are its sources. Three fourth of the earth is in the form of ocean water and a huge reservoir of water do exist underground (Barthwal., 2009).

Oil spillage, often results from accidental or operational discharges of petroleum hydrocarbon in to the environment, during the operations of the oil and gas industries. The inadvertent discharges of petroleum hydrocarbons into the environment often pose threats to human health, safety and the environment, and have significant socio-economic consequences. Evidence of acute and chronic toxicity demonstrates the potential toxic and negative impacts of petroleum-derived wastes on the tropical environment (Holdway., 2002).

Soils and underground water is the ultimate sink for most petroleum contaminants, such as Benzene, Toluene, Ethylbenzene, and Xylenes (BTEX) and Total Petroleum Hydrocarbon (TPH). These compounds are some of the volatile organic compounds, found in petroleum derivatives.

Environmental Guidelines and Standards for the Petroleum Industry in Nigeria standards for soil and groundwater are also presented in table below.

Table 1 EGASPIN target and intervention values for soil and groundwater (UNEP, 2011)

Substance	Soil/sediment #		Groundwater	
	Target value	Intervention value	Target value	Intervention value
A. Aromatic compounds	(mg/kg dry material)		(µg/l)	
Benzene	0.05	1	0.2	30
Ethyl benzene	0.05	50	0.2	150
Phenol	0.05	40	0.2	2,000
Toluene	0.05	130	0.2	1,000
Xylene	0.05	25	0.2	70
B. Metals				
Barium	200	625	50	625
E. Other pollutants				
Mineral oil	50	5,000	50	600

The values given for soil are for 20 % soil organic matter with a formula given for calibrating for other soil organic matter concentrations

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In-situ groundwater bioremediation can be effective for the full range of petroleum hydrocarbons. Bioremediation generally requires a mechanism for stimulating and maintaining the activity of these microorganisms. This mechanism is usually a delivery system for providing one or more of the following: An electron acceptor (oxygen, nitrate); nutrients (nitrogen, phosphorus); and an energy source (carbon). Generally, electron acceptors and nutrients are the two most critical components of any delivery system (USEPA., 2014). In-situ treatment technologies are conventionally used in the oil and gas industry to foster the application of bio-nutrient, for the remediation of petroleum hydrocarbon contaminated underground water.

However, the use of different types of bio-nutrient, has given rise to diverse technological method of application, based on peculiarity. This therefore distinguishes one application approach from another. For the purpose of this study, the concept of an activated persulfate oxidant (bionutrient), as presented in this study will require a direct application Technique. Application of activated persulfate is the ideal solution to address groundwater contamination because of its ability to treat a wide range of recalcitrant contaminants. When properly activated, persulfate oxidant provides an unmatched combination of oxidative power and control that can be delivered both safely and cost effectively. This study/pilot test will also consider the effect and extent of remediation achieved by the proffered bionutrient.

Gas Chromatography (GC) fingerprinting was employed. A gas chromatograph is a chemical analysis instrument for separating chemicals in a complex sample (Wikipedia, 2014). It is a laboratory technique that separates mixtures into individual components. It is used to identify components and to measure their concentrations.

Objective of Study

This study seeks to;

1. Ascertain the Total Petroleum Hydrocarbon (TPH) concentration, Benzene, Toluene, Ethylbenzene and Xylenes (BTEX) concentration in the contaminated field.
2. Demonstrate the effectiveness of an activated persulfate oxidant (bionutrient) and its direct applications technique in bio-remediating petroleum hydrocarbon contaminated underground water in the Niger Delta field below the DPR detection limit.
3. Evaluate the performance of the bio-treatment technology. This would be achieved by sampling the underground water, before and after remediation.

Background of study

Oil spills in the Niger Delta have been a regular occurrence, and the resultant degradation of the surrounding environment has caused significant tension between the people living in the region and the multinational oil companies operating there. It is only in the past decade that environmental groups, the Federal

Government, and the foreign oil companies operating in the Niger Delta began to take steps to mitigate the impacts. Large areas of the mangrove ecosystem have also been destroyed. The mangrove forest was in the past a major source of wood for the indigenous people. In some places it is no longer in a healthy state to sustain this use (Nwilo and Badejo 2005).

When a particular field or site is heavily impacted and the soil and/or underground water is polluted, it becomes absolutely important to remediate such field, so as to salvage the environment from further damage. This has given rise to the exploitation of various bioremediation technologies by government agencies and producing companies within the area. The goal of remediating the vast spill site in the Niger Delta can be achieved by maximizing the use of direct application technique, over an activated persulfate oxidant (bionutrient) as an underground water bioremediation technique

MATERIALS AND METHODS

The site underground water was contaminated with petroleum hydrocarbon. The process of bioremediation, from start to finish took a period of 28 weeks. Underground water sample was taken at a depth of 3.0-4.5metres.

A hand auger was used to drill to the determined depth and a bail used to collect water into sample containers, free from hydrocarbon contamination. The data sets, to be analyzed include; TPH (total petroleum hydrocarbon),and BTEX (benzene, toluene, ethylbenzene, and xylenes). These physiochemical parameters were monitored before and after remediation.

Direct application technique will be employed with the use of an activated persulfate oxidant (bionutrient). The direct application technique involved:

1. *Site Investigation:* Site investigations to characterize the site geology and hydrology, geochemical conditions, and nature and extent of contamination.
2. *Underground water Sampling and Analysis:* Underground water samples were taken from the pilot test site before remediation commenced from 3-4.5 meters depth at three spots (A, B and C). The spots coordinates were marked using a GPS and samples were taken using a bail into sample containers, free from hydrocarbon contamination. The water samples were taken for immediate physico-chemical analysis.
3. *Deep Excavation to Water Level:* The contaminated soil was excavated to a depth of 4.5metres, to expose the impact at the water table. This was done using heavy duty equipment (Excavator).
4. *Addition of Bionutrient:* Application of an activated per sulfate oxidant was done at the water table by manual broadcasting. Each 55.1lb of per sulfate oxidant was lime activated, and then hand broadcasted directly on the water table.
5. *Back Filling:* After a period of 2days, the excavated soil, blended with an activated per sulfate oxidant

and top soil is backfilled after treatment and is distributed evenly on the site.

6. **Soil Sampling and Analysis:** Underground water samples were taken from the pilot test site after remediation, at the 28th week and from 3.0-4.5 meters depth. These samples were taking from the initial marked GPS coordinates (Well 1, 2 and 3), into sample containers, free from hydrocarbon contamination. The underground water samples were taken for immediate physico-chemical analysis.

Results (data) for the soil/underground water analysis will be collected under an established partnership with.

The sample result for the analyzed underground water collected before and after bioremediation will be tabulated and component concentration was measured using Gas Chromatography (GC) fingerprint.

RESULTS

Sample Characteristics before remediation (water)

Table 2 Physical analysis of water sample from Well 1 before remediation

Depth	Coordinate	Characteristics
4.2m	N: 04°41'50.3"	Presence of Hydrocarbon at the surface of the water
Water level:1.3m	E: 007°14'37.8"	

Table 3 Physical analysis of water sample from Well 2 before remediation

Depth	Coordinate	Characteristics
4.3m	N: 04°41'50.4"	Presence of Hydrocarbon at the surface of the water
Water level:0.7m	E: 007°14'37.1"	

Table 4 Physical analysis of water sample from Well 3 before remediation

Depth	Coordinate	Characteristics
4.3m	N: 04°41'50.5"	No Presence of Hydrocarbon at the surface of the water
Water level:0.8m	E: 007°14'36.8"	

Table 5 Report for Well 1-3 (Water)

S/no	Parameter	Sample point/depth	Sample type	Concentration	Dpr intervention value	Detection limit
1	TPH (ug/l)	(Well 1)	WATER	2682.596ug/l	600ug/l	0.0001ug/l
		(Well 2)		219533.00ug/l		
		(Well 3)		BDL		
(BTEX) PROFILE						
1	Benzene	(Well 1)	WATER	845.60ug/l	30ug/l	0.001ug/l
2	Toluene			100.00ug/l	1000ug/l	
3	Ethylbenzene			36.62ug/l	150ug/l	
4	m,p-xylene			116.42ug/l	2000ug/l	
5	o-xylene			76.75ug/l	70ug/l	
1	Benzene	(Well 2)	WATER	908.80ug/l	30ug/l	0.001ug/l
2	Toluene			73.00ug/l	1000ug/l	
3	Ethylbenzene			12.96ug/l	150ug/l	
4	m,p-xylene			65.74ug/l	2000ug/l	
5	o-xylene			35.74ug/l	70ug/l	
1	Benzene	(Well 3)	WATER	BDL	30ug/l	0.001ug/l
2	Toluene			BDL	1000ug/l	
3	Ethylbenzene			BDL	150ug/l	
4	m,p-xylene			BDL	2000ug/l	
5	o-xylene			BDL	70ug/l	

Laboratory Analytical Report before Remediation.

Gas Chromatography Fingerprint (GCF) Chart for Water Sample Before Remediation.



Fig 1 Hewlett-Packard – HP 6890 GC System

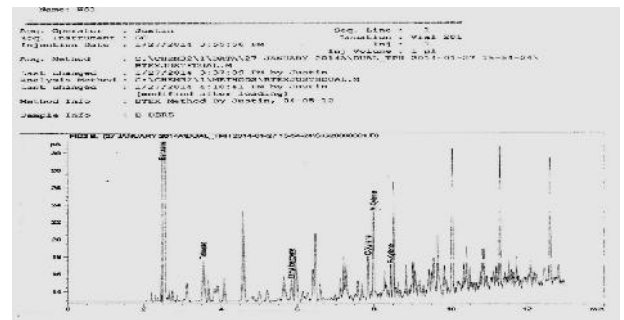
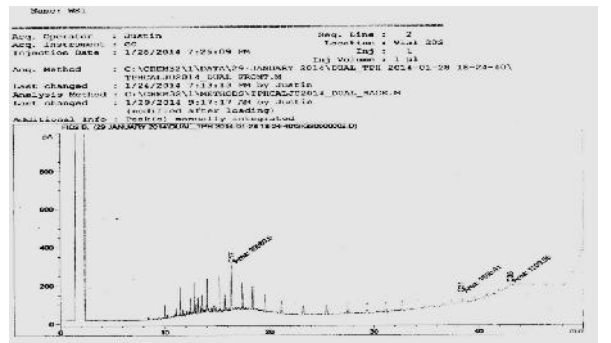


Fig 2 GCF of Well 1 water Sample (BTEX and TPH)

Sample Characteristics After Remediation (water)

Laboratory Analytical Report after Remediation

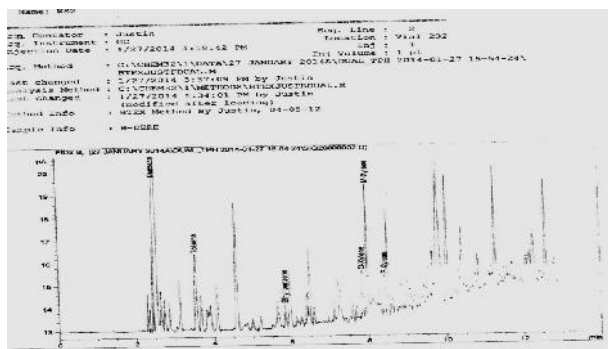


Fig 3 Showing GC F of Well 2 water Sample (BTEX and TPH).

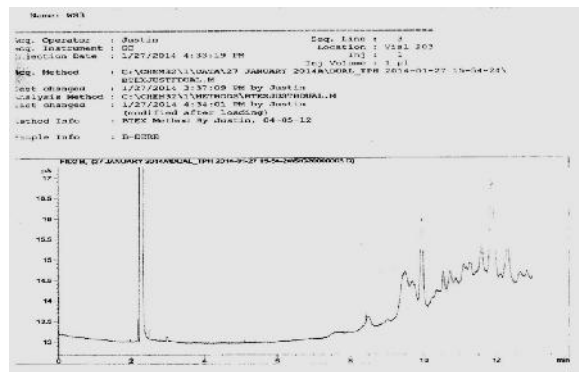


Fig 4 Showing GCF of Well 3 water Sample (BTEX and TPH)

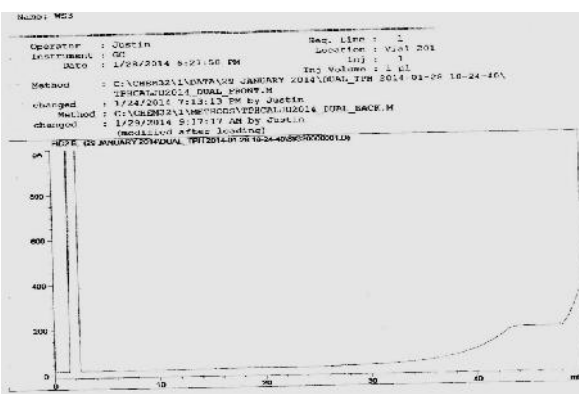
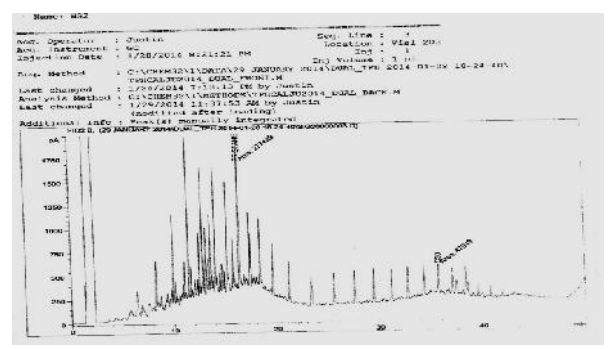


Fig 4 Showing GCF of Well 3 water Sample (BTEX and TPH)

Table 6 Physical analysis of water sample from well 1-3 after remediation

Depth	Coordinate	Characteristics (well 1)
4.2m	N: 04°41'50.3"	Clean no hydrocarbon smell, no visible presence of hydrocarbon contamination.
Water level:1.3m	E: 007°14'37.8"	
Depth	Coordinate	Characteristics (well 2)
4.3m	N: 04041'50.4"	Clean no hydrocarbon smell, no visible presence of hydrocarbon contamination.
Water level:0.7m	E: 007014'37.1"	
Depth	Coordinate	Characteristics (well 3)
4.3m	N: 04041'50.5"	Clean no hydrocarbon smell, no visible presence of hydrocarbon contamination.
Water level:0.8m	E: 007014'36.8"	

Gas Chromatography Fingerprint (GCF) Chart for Water Sample



Table 7Report for Well 1-3 (Water)

S/no	Parameter	Sample point/depth	Sample type	Concentration	Dpr intervention value	Detection limit
1	TPH (ug/l)	(Well 1)	WATER	158.24ug/l	600ug/l	0.0001ug/l
		(Well 2)		132.28ug/l		
		(Well 3)		892.32ug/l		
(BTEX) PROFILE						
1	Benzene	(Well 1)	WATER	BDL	30ug/l	0.001ug/l
2	Toluene			BDL	1000ug/l	
3	Ethylbenzene			BDL	150ug/l	
4	m,p-xylene			BDL	2000ug/l	
5	o-xylene			BDL	70ug/l	
1	Benzene	(Well 2)	WATER	BDL	30ug/l	0.001ug/l
2	Toluene			BDL	1000ug/l	
3	Ethylbenzene			BDL	150ug/l	
4	m,p-xylene			BDL	2000ug/l	
5	o-xylene			BDL	70ug/l	
1	Benzene	(Well 3)	WATER	BDL	30ug/l	0.001ug/l
2	Toluene			BDL	1000ug/l	
3	Ethylbenzene			BDL	150ug/l	
4	m,p-xylene			BDL	2000ug/l	
5	o-xylene			BDL	70ug/l	

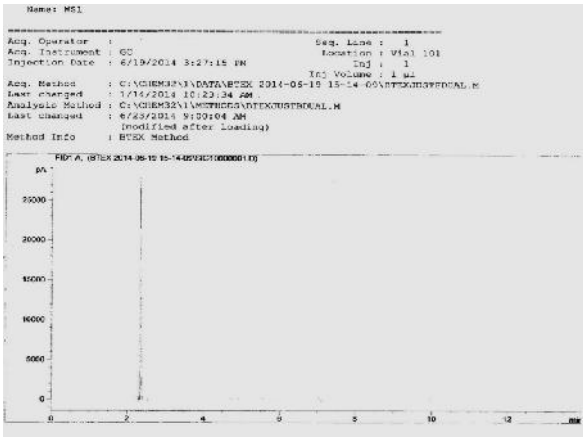


Fig 5 Showing GCF of Well 1 water Sample after Remediation (BTEX and TPH)

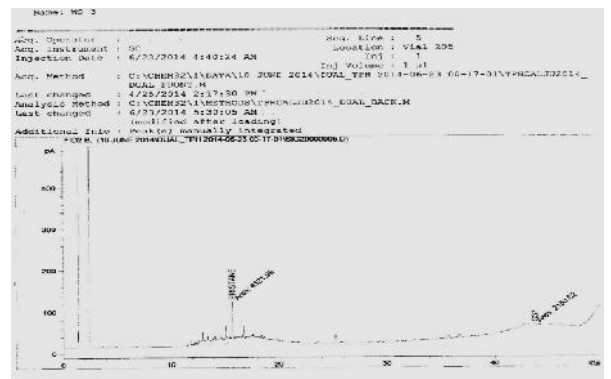


Fig 7 Showing GCF of Well 3 water Sample after Remediation (TPH and BTEX)

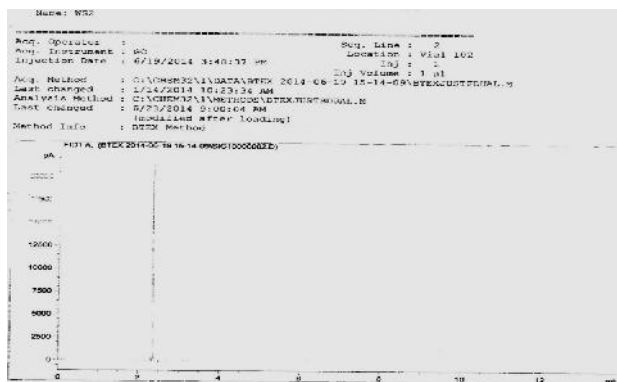
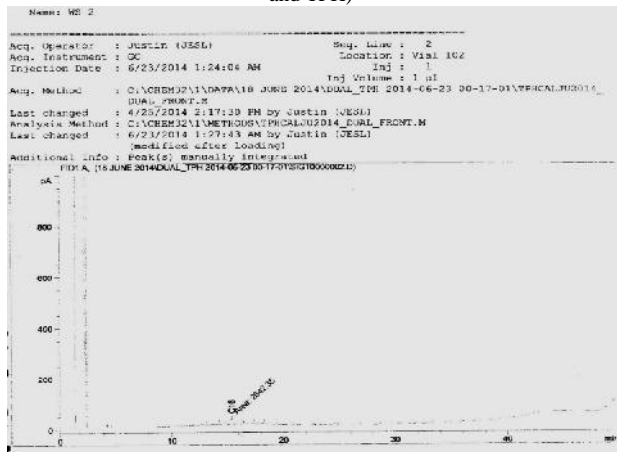
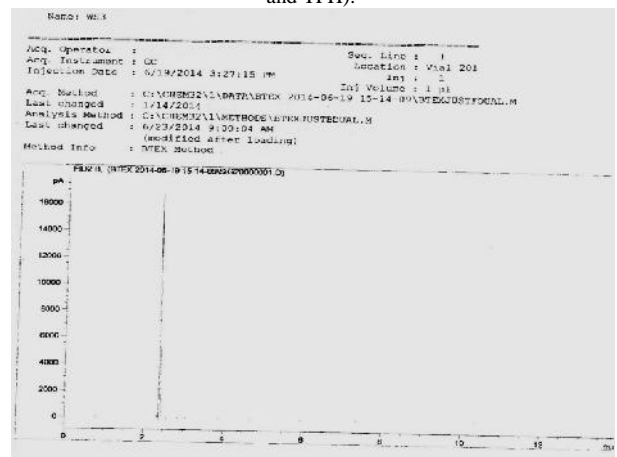


Fig 6 Showing GCF of Well 2 water Sample after Remediation (BTEX and TPH).



DISCUSSIONS OF RESULTS

Significant changes were observed, while making comparison between the contaminant concentration and chromatography fingerprint of the underground water before and after bioremediation took place. Also there has been a reduction of these organic petroleum hydrocarbon contaminants below detection limit and the DPR intervention value.

Before remediation, gas chromatograph-flame ionization detector (GC-FID) fingerprints of the aliphatic fractions (C12-C40, see figure 2-7) revealed that the oil was a fresh and unweathered crude oil. An analogous series of n-alkanes are clearly visible, indicating relatively fresh oil. Below the marks of the fingerprints, a small unresolved complex mixture can be seen, indicating the presence of some weathered material. But after remediation, gas chromatography fingerprints supports the laboratory analytical report to prove that the oil and series of n-alkanes (TPH and BTEX profile) have been biodegraded (see figure 2-7).

Underground Water

Underground water in this area has been polluted, with maximum TPH concentrations throughout the considered wells being 219533.00ug/l and 2682.596ug/l in well 2 and well 1 respectively. While the concentration of the BTEX (Profile), at well 1 benzene is 908.80ug/l (above detection limit and DPR intervention value), toluene is 73.00ug/l (above detection limit and below DPR intervention value), ethylbenzene is 12.96ug/l (above detection limit and below DPR intervention value), m,p-xylene is 65.74ug/l (above detection limit and below DPR intervention value) and o-xylene is 35.74ug/l (above detection limit and below DPR intervention value). (See table 5).

At well 1 we had the initial TPH to be 2682.596ug/l but after remediation the concentration reduced drastically to 158.242ug/l which is below the DPR intervention value. Also the BTEX (Profile) which were initially of high concentration, reduced below detection limit (See table 5 and 7). It can be said that at well 1 the underground water is clean.

At well 2 we had the initial TPH to be 219533.0ug/l at concentration the water is highly contaminated, but after remediation there was a drastic reduction of TPH to 132,28ug/l,

far below DPR intervention value. Also the BTEX (Profile) which were initially of a high concentration, reduced below detection limit (See table 5 and 7). This demonstrates an efficient remediation of polluted underground water.

Mathematically, to ascertain the percentage of biodegradation we would check for the percentage of contaminants destroyed by using;

$$\% \text{ contaminant destroyed} = \frac{[\text{contaminant}] \text{ initial} - [\text{contaminant}] \text{ final}}{[\text{contaminant}] \text{ initial}} * 100$$

Solving with the values in the table and the above formula, it is observed that there was a significant biodegradation of the TPH concentration, **in well 1 and 2 we had 94% and 100% respectively**. For the BTEX profile, there was a **100% biodegradation** achieved all through the wells.

However, at well 3 initial laboratory analytical report shows that like TPH is below detection limit and the BTEX (Profile) also is below detection limit. However there was surprising increase in the TPH at well 3 after remediation above DPR intervention value, the TPH rose to 892.32ug/l and the BTEX (Profile) remained below detection limit. (See table 5&7).

The sudden increase in TPH at well 3 was as a result of migration. Petroleum hydrocarbon from other surrounding contaminated site migrated through the underground water flow regime into the site being remediated, thereby altering the initial clean state of the water.

See graphical representation of TPH/BTEX concentration before and after remediation:

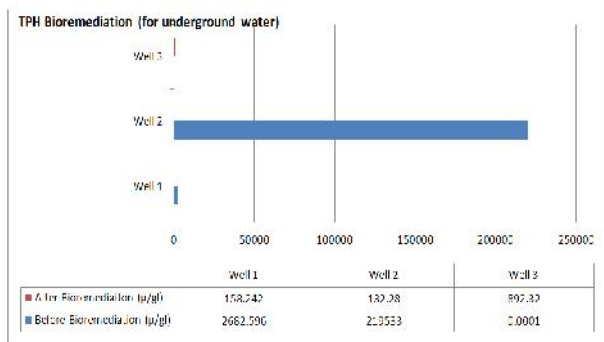


Fig. 8 TPH Bioremediation for Underground Water

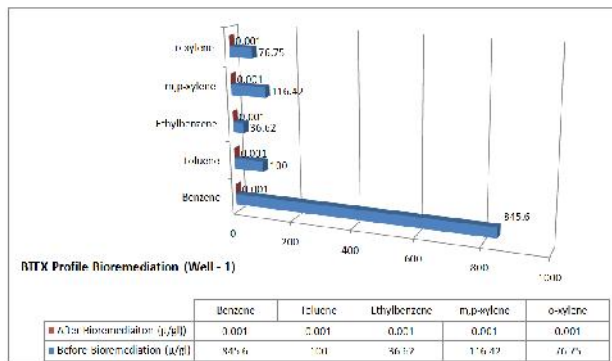


Fig. 9 BTEX Bioremediation Profile for Well - 1

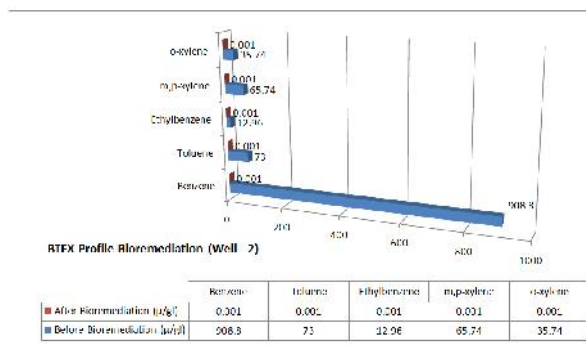


Fig. 10 BTEX Bioremediation Profile for Well - 2

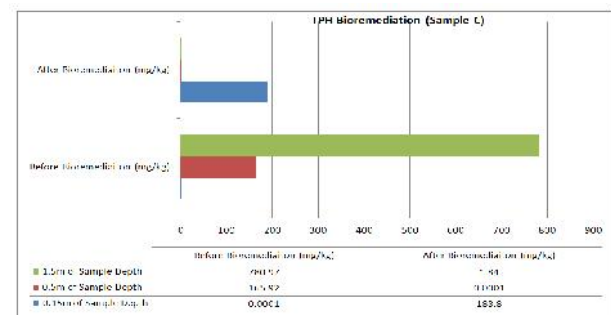
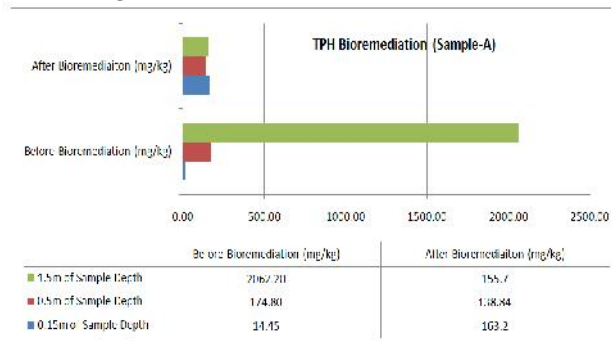


Fig. 11 TPH Bioremediation Profile for Well-3 (Sample C)



Figure 12 Showing assessment of underground water in a trial pit.





Figure 13 Showing sample of contaminated underground water being collected.



Figure 14 Showing backfilling of excavated soil, after direct application of bionutrient on the surface of the exposed underground water.



Figure 15 Showing sample of underground water collected after bioremediation.

CONCLUSION AND RECOMMENDATION

The quality of underground water remain a matter of great concern, hence it must be kept at an acceptable standard.

How to cite this article:

Ohia, Nnaemeka, Iyiegbo and Hillary., Petroleum Hydrocarbon Underground Water Bioremediation Using Direct Application Technique, Of Abionutrient: A Niger Delta Case. *International Journal of Recent Scientific Research Vol. 6, Issue, 8, pp.5704-5710, August, 2015*

Petroleum hydrocarbon bioremediation using soil blending technique over an activated persulfate oxidant has shown great promise, in its effectiveness and comparatively inexpensive rate. Also in comparison to other conventional technologies used for groundwater remediation, the cost of drilling injection wells and setting up complex processes and designs has been knocked out. Further researches in this area can result in the development of most efficient and less time consuming technologies. Also, further research is critical to investigate the cause and proffer solution to the underground water migration of contaminants from other polluted site into the site being remediated.

Recommendation

- Underground water should be treated at its point of use.
- During site (soil and underground water) remediation surrounding contaminated site should be barred or containment should be initiated by physically using an underground barrier of clay, cement or steel. Containment can also be initiated chemically by imploring chemical reactive substances to immobilize contaminants from migrating from surrounding contaminated site, into the site being remediated.
- Oil and gas firms should use best management practices to reduce or prevent instances of oil spill. This can be done by routine maintenance of oilfield facilities and prevention of illegal activities.

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